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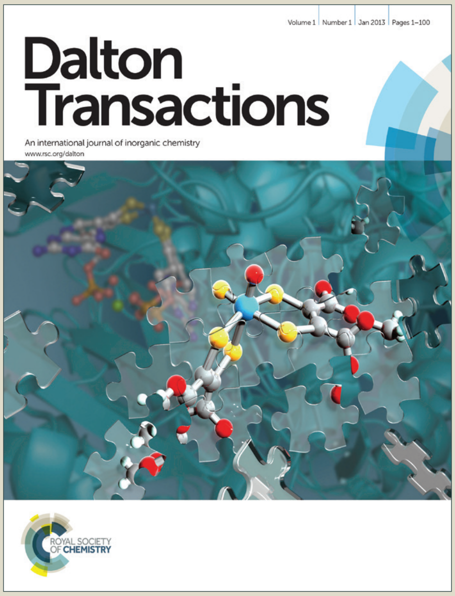

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Syntheses, structures and flexible coordination of sterically demanding di- and "tri"-lithiated methandiides

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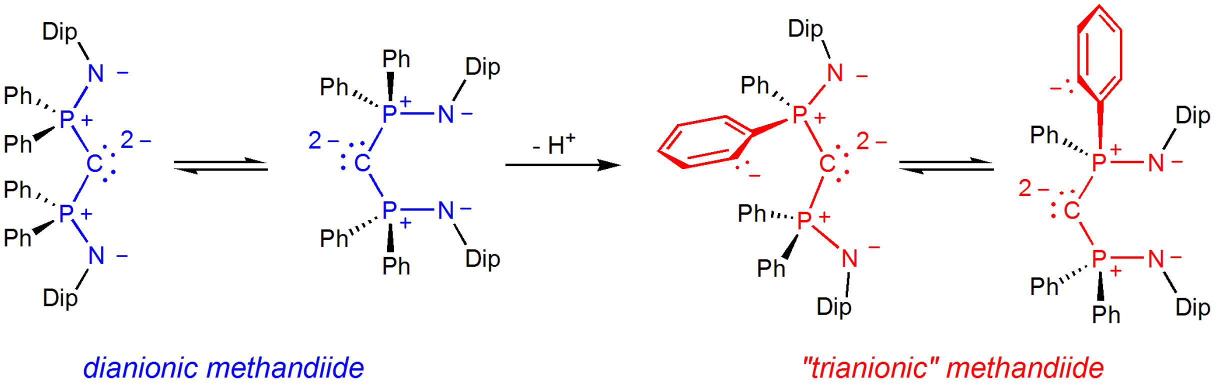

Sequential lithiation of a sterically demanding bis(iminophosphoranyl)methane afforded di- and trianionic methandiide lithium complexes and their structures and coordination behaviour have been studied with solid state and solution methods.

Syntheses, structures and flexible coordination of sterically demanding di- and “tri”-lithiated methandiides

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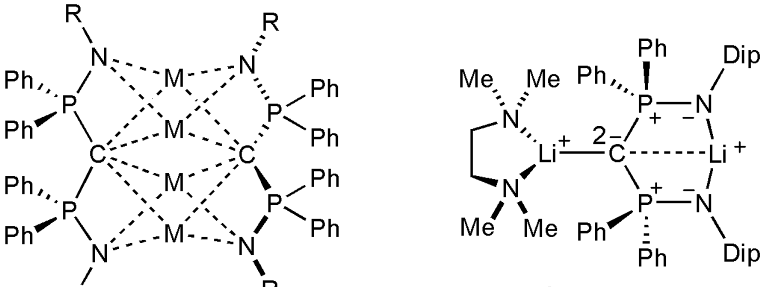
Lithiation of the sterically demanding bis(iminophosphoranyl)methane $H_2C\{Ph_2P(=NDip)\}_2$ (Dip = 2,6-$i$$Pr_2C_6H_3$), H_2L, with alkyllithium reagents afforded the methandiide complexes $[(LLi_2)_2]$ **2**, $[LLi_2(OEt_2)_2]$ **4**, $[LLi_2(THF)_3]$ **5**, $[LLi_2(THF)_2]$ **6**, and $[LLi_2(PMDTA)]$ **7** (PMDTA = *N*,*N*,*N′*,*N″*,*N″*-pentamethyldiethylenetriamine), from various solvents or after the addition of donor molecules. The complex $[HC(Ph_2PNDip)(Ph_2P)Li(THF)_2]$ **3** was further identified as a by-product under certain conditions. Further lithiation of the methandiide in ortho-position of one P-bound phenyl group affords complexes of the trianionic ligand L'^{3-}, and the complexes $[(L'Li_3)_2]$ **8** and $[L'Li_3(THF)_4]$ **9** were obtained. Different isomeric forms for the methandiide units investigated in solution and in the solid state are described, and the crystal structures of complexes **2**, **3**, and **5**-**9** are reported.

Introduction

Methandiides represent a popular ligand class with a rare central, formally dianionic carbon centre that forms numerous complexes with elements from across the periodic table and show diverse M-C bonding arrangements.[1] These methandiides are typically accessible from the corresponding substituted methanes, *e.g.* bis(iminophosphoranyl)methanes, and very strong bases. The resulting complexes often show unexpected bonding and coordination modes and are a convenient source of methandiides for metathesis chemistry. A large range of bis(iminophosphoranyl)methanide and methandiide alkali metal complexes has been prepared[2] and solvent-free examples generally adopt the general dimeric structure shown in scheme 1. Most examples have been prepared with N-bound trimethylsilyl, adamantyl, phenyl or mesityl substituents and convenient access to sterically more demanding derivatives is limited. In this realm, the reaction of H_2L (= $H_2C\{Ph_2P(=NDip)\}_2$, Dip = 2,6-iPr$_2$C$_6$H$_3$) with two equivalents of *tert*-butyllithium and the addition of TMEDA (*N,N,N′,N′*-tetramethylethylenediamine) previously afforded the unusual dilithium methandiide complex **1**[2c] (see scheme 1) which features an ionic (TMEDA)Li-carbon bond from an almost exclusively carbon based p-orbital, and a relatively short contact of the second, *N,N′*-chelated Li^+ ion to the central carbon centre. The resulting geometry approaches an overall trans-planar four-coordinate carbon atom. Here we report on a series of di- and “tri”-lithiated methandiide complexes based on L^{2-} and shed some light on their flexible coordination behaviour with solid state structures and solution studies.



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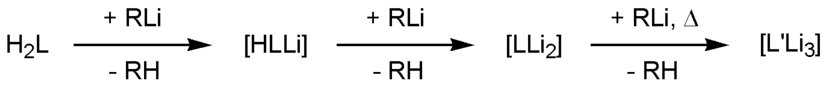
Scheme 1 Common molecular structure of bis(iminophosphoranyl)methandiide alkali metal complexes, left, M = alkali metal; and [LLi$_2$(TMEDA)] **1**, Dip = 2,6-iPr$_2$C$_6$H$_3$.

Results and Discussion

Treating the bis(iminophosphoranyl)methane H_2L with one equivalent of *n*-butyllithium in a hydrocarbon solvent results in the clean formation of the previously reported monomeric complex

[HLLi][2c] in good yield. Similarly, this first lithiation step can be carried out in some coordinating solvents. Treating H_2L with two equivalent of *n*-butyllithium in benzene afforded up to 47% of the colourless methandiide $[(LLi_2)_2]$ **2** isolated by crystallization, see scheme 2 for a simplified reaction sequence.



$$H_2L \xrightarrow[-\ RH]{+\ RLi} [HLLi] \xrightarrow[-\ RH]{+\ RLi} [LLi_2] \xrightarrow[-\ RH]{+\ RLi,\ \Delta} [L'Li_3]$$

$[LLi_2]$: $[(LLi_2)_2]$ **2**, $[LLi_2(OEt_2)_3]$ **4**, $[LLi_2(THF)_3]$ **5**, $[LLi_2(THF)_2]$ **6**, $[LLi_2(PMDTA)]$ **7**

$[L'Li_3]$: $[(L'Li_3)_2]$ **8**, $[L'Li_3(THF)_4]$ **9**

Scheme 2 Lithiation sequence of H_2L and composition of compound **2**, **4-9**; PMDTA = *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine.

Both toluene and benzene solvates of $[(LLi_2)_2]$ **2** have been structurally characterized, see Fig. 1 and Fig. S1, respectively, for images and selected bond lengths and angles. In **2**·2 C_7H_8 (Fig. 1), a full molecule is present in the asymmetric unit and shows the expected L_2Li_4 cluster albeit with a less symmetrical overall structure compared with derivatives having smaller N-bound substituents.[2] Solvate **2**·4 C_6H_6 (see Fig. S1) shows the same overall structure, but with half a molecule in the asymmetric unit and severe disorder of the Li^+ positions. One Li^+ ion, Li4 in **2**·2 C_7H_8 and Li1 in **2**·4 C_6H_6, is predominantly bridging between two N-atoms with additional short contacts to the Dip-ipso-carbons and no short contact to a methandiide carbon atom. Two Li^+ ions (Li1 and Li2 in **2**·2 C_7H_8) are essentially coordinated to two N and one methandiide carbon atom each, and another Li^+ (Li3 in **2**·2 C_7H_8) ion is mainly coordinated to two methanide carbons and one N-atom. The shortest Li-C contacts in **2**·2 C_7H_8 are ranging from 2.115(3) to 2.420(3) Å. Once crystallized, all solvates of $[(LLi_2)_2]$ **2** show a very limited solubility in uncoordinating solvents such as benzene. Even at elevated temperatures of 60°C, no meaningful $^{13}C\{^1H\}$ NMR data could be recorded. The ^1H NMR spectrum shows four doublets and two septets for the isopropyl protons and a broadened $^{31}P\{^1H\}$ NMR resonance at 22 ppm is found.

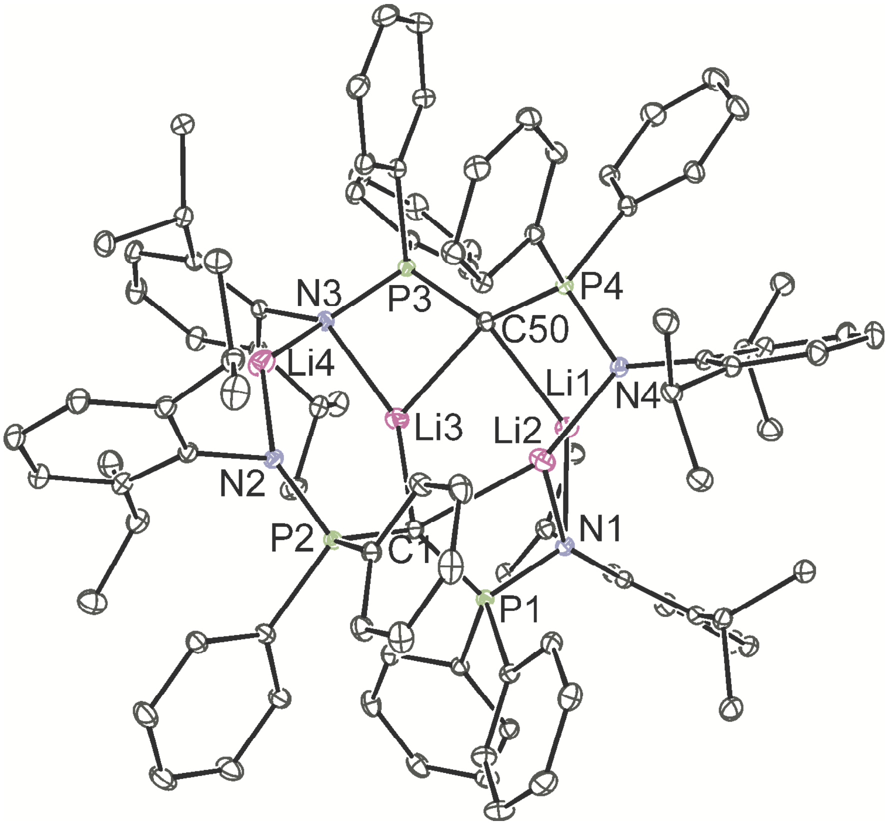


Fig. 1 Molecular structure of compound **2**·2 C_7H_8 (30% probability thermal ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)-C(1) 1.6872(16), C(1)-P(2) 1.7058(16), P(1)-N(1) 1.6456(14), P(2)-N(2) 1.6326(14), P(3)-C(50) 1.6948(16), P(4)-C(50) 1.6994(16), P(3)-N(3) 1.6496(14), P(4)-N(4) 1.6433(14), N(1)-Li(1) 2.137(3), N(1)-Li(2) 2.015(3), C(1)-Li(3) 2.115(3), C(1)-Li(2) 2.420(3), Li(1)-N(4) 2.061(3), Li(1)-C(50) 2.261(3), N(2)-Li(4) 1.899(3), Li(2)-N(4) 2.055(3), N(3)-Li(4) 1.948(3), N(3)-Li(3) 2.129(3), Li(3)-C(50) 2.218(3); P(1)-C(1)-P(2) 128.80(9), P(3)-C(50)-P(4) 124.68(9), Li(3)-C(1)-Li(2) 79.14(12), Li(3)-C(50)-Li(1) 81.73(12), N(2)-Li(4)-N(3) 132.48(18).

The reaction of H_2L with 2.0 to 2.3 equivalents of *n*-butyllithium was also carried out in toluene at various temperatures and $[(LLi_2)_2]$ **2** could be formed and isolated, albeit in somewhat lower and varying yields, and a number of by-products are formed, including [HLLi].[2c] The toluene solution after isolation of crystallized **2** contained in one case a mixture with a main product that shows two very broad doublet resonances at δ -22.3 ppm and δ 25.1 ppm (J_{PP} = 103 Hz) in its $^{31}P\{^1H\}$ NMR spectrum, and the asymmetric lithium methanide $[HC(Ph_2PNDip)(Ph_2P)Li(THF)_2]$ **3** could be isolated as colourless crystals, see Fig. 2, after recrystallization from *n*-hexane and THF. In **3**, one P^V centre is reduced to a P^{III} fragment possibly from the reaction with excess alkyllithium reagent before the second deprotonation of [HLLi] could proceed. The methanide N,P-chelates the Li ion and forms a five-membered ring system. The Li^+ cation is further coordinated by two THF ligands. Asymmetric phosphinyl-iminophosphoranyl-methanides of Li,[2j] in a mixed ligand system, and K,[3] in [K{$Ph_2PCHPPh_2(NSiMe_3)$}], have previously been structurally characterized and the latter shows a different N,C-coordination mode compared with **3**. Complex **3** shows one doublet and one septet for the protons of the isopropyl group and a doublet of a doublet with $J_{\mathrm{PH,PH}}$ coupling constants of 14.4 Hz and 6.9 Hz, respectively, for the proton bound to the $P^{V}CP^{III}$-methanide centre. Very similar values were found for the respective proton in [K{$Ph_2PCHPPh_2(NSiMe_3)$}].[3] The $^{31}P\{^1H\}$ NMR spectrum for the P^{III} centre of **3** reveals a doublet of a 1:1:1:1-quartet for the ^{7}Li-isotopomer (*ca.* 93%) at δ -21.1 ppm and a partially overlayed doublet of a 1:1:1-triplet for the ^{6}Li-isotopomer (*ca.* 6%), respectively, and a doublet at δ 24.0 for the P^{V} centre. Coupling constants are found to be $^3J_{\mathrm{PP}}$ = 117 Hz and $^1J_{\mathrm{P}^7\mathrm{Li}}$ = 39 Hz; the $J_{\mathrm{P}^6\mathrm{Li}}$ is not resolved due to signal overlapping. Accordingly, the $^7Li\{^1H\}$ NMR spectrum shows a doublet for coupling to the P^{III} atom.

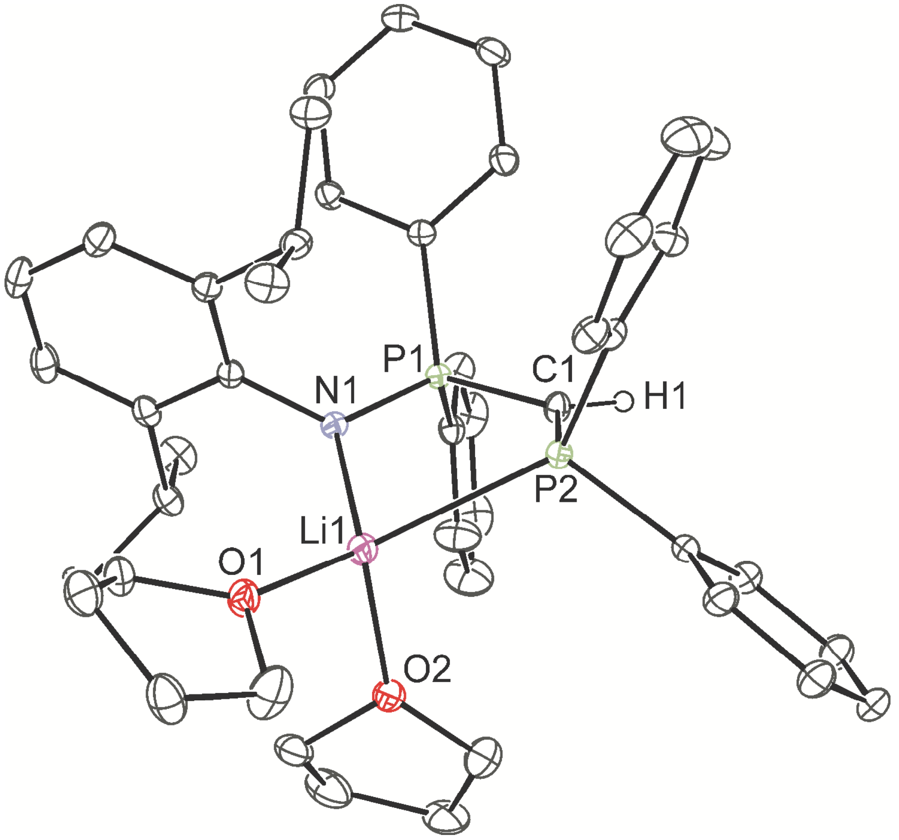


Fig. 2 Molecular structure of compound [HC(Ph_2PNDip)(Ph_2P)Li(THF)$_2$] **3** (30% probability thermal ellipsoids). Hydrogen atoms except H1 have been omitted for clarity. Only the main part of one disordered THF molecule is shown. Selected bond lengths (Å) and angles (°): P(1)-N(1) 1.6016(11), P(1)-C(1) 1.7031(13), C(1)-P(2) 1.7415(13), O(1)-Li(1) 1.944(3), Li(1)-O(2) 1.939(8), N(1)-Li(1) 1.973(3), Li(1)-P(2) 2.609(2); N(1)-P(1)-C(1) 111.28(6), P(1)-C(1)-P(2) 120.03(8), N(1)-Li(1)-P(2) 87.00(9), O(2)-Li(1)-O(1) 96.5(5).

H_2L can also be doubly deprotonated with methyllithium in diethyl ether at room temperature to give an orange-amber solution. Work-up using hydrocarbon solvents afforded colourless crystalline $[LLi_2(OEt_2)_2]$ **4**. If the reaction is carried out first in diethyl ether and THF is added for work-up, crystals of yellow $[LLi_2(THF)_3]$ **5** and colourless $[LLi_2(THF)_2]$ **6** could be isolated under different conditions. The crystal structure of $[LLi_2(THF)_3]$ **5** is shown in Fig. 3 and that of $[LLi_2(THF)_2]$ **6** in Fig. 4. Diffraction experiments on a colourless crystal of $[LLi_2(OEt_2)_2]$ **4** showed it to have the same overall structure as that for $[LLi_2(THF)_2]$ **6**, but the data was of too poor quality to be reported in here. The methandiide fragments L^{2-}, see scheme 3, can be described as having either an isomeric W-form (as in **4** and **6**), with two four-membered chelate rings around a central, spirocyclic carbon atom, or an isomeric U-form (as in **5** and **1**), forming a six-membered chelate ring, plus further lithium-carbon bond. The least-square planes of the two four-membered N,P,C,Li-heterocycles in **6** are almost orthogonal to each other and intersect at an angle of *ca.* 74°. In contrast, the two Li cations and the N, P and central carbon atom of the methandiide unit in **5** (and **1**) are almost planar. With coordination of an additional THF molecule, W-form **6** changes to U-form **5**. The one unsupported carbon-lithium bond in **5** (2.050(4) Å) is significantly shorter than the two carbon-lithium contacts (2.112(5) and 2.144(5) Å) at the spirocyclic C-centre in **6**, and the comparable, unsupported (TMEDA)Li-C distance (2.124(3) Å) in **1**.[2c]

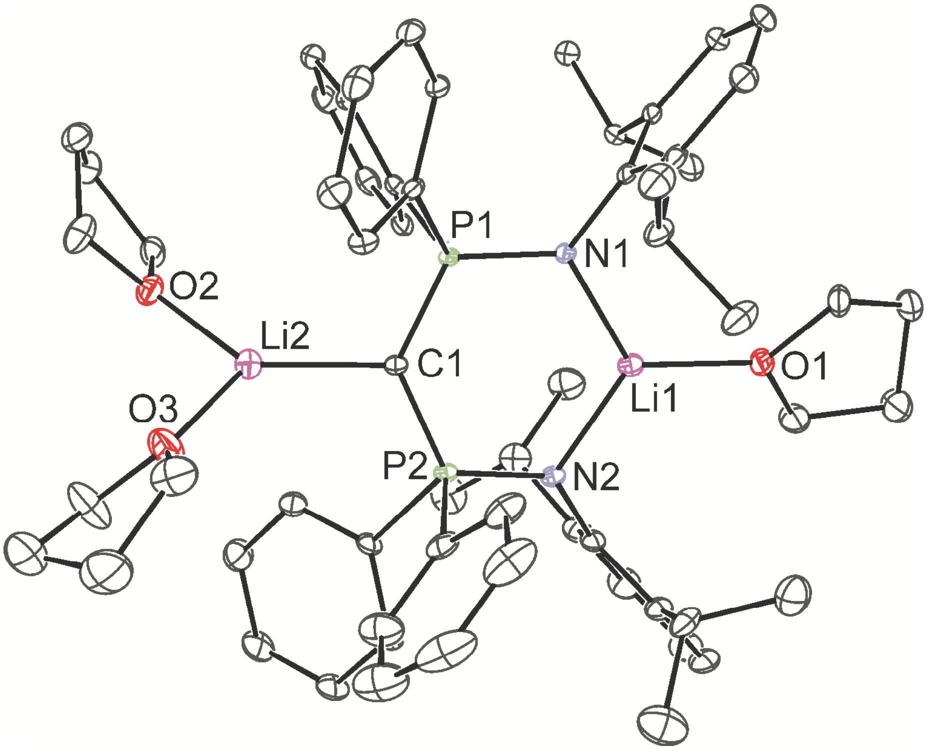


Fig. 3 Molecular structure of compound **5** (30% probability thermal ellipsoids). Hydrogen atoms and a second independent molecule with similar geometrical features in the asymmetric unit have been omitted for clarity. Selected bond lengths (Å) and angles (°) of the first molecule: P(1)-N(1)

1.6221(16), P(2)-N(2) 1.6145(17), P(1)-C(1) 1.661(2), P(1)-C(2) 1.8449(19), O(1)-Li(1) 1.962(4), N(1)-Li(1) 1.915(3), C(1)-P(2) 1.6609(18), C(1)-Li(2) 2.050(4), Li(1)-N(2) 1.916(4), O(2)-Li(2) 1.922(4), Li(2)-O(3) 1.901(4); P(2)-C(1)-P(1) 128.89(12), N(1)-Li(1)-N(2) 113.42(18), O(3)-Li(2)-O(2) 98.66(18).

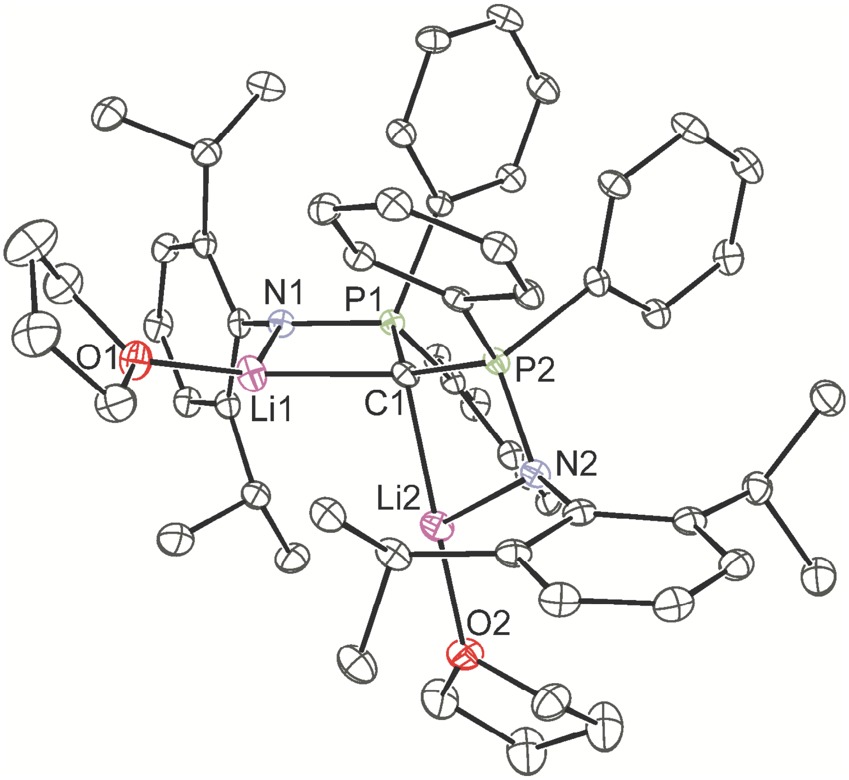
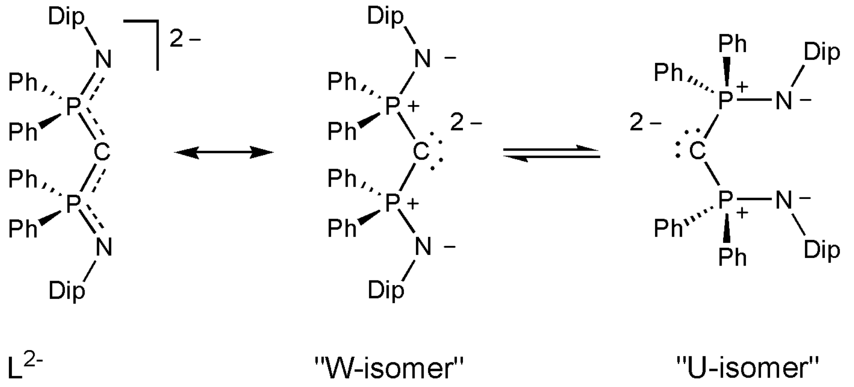


Fig. 4 Molecular structure of compound **6** (30% probability thermal ellipsoids). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)-N(1) 1.615(2), P(2)-N(2) 1.620(2), P(1)-C(1) 1.683(2), C(1)-P(2) 1.689(2), O(1)-Li(1) 1.888(5), O(2)-Li(2) 1.904(5), N(1)-Li(1) 1.942(5), N(2)-Li(2) 1.943(5), C(1)-Li(1) 2.112(5), C(1)-Li(2) 2.144(5); N(1)-P(1)-C(1) 105.66(11), N(2)-P(2)-C(1) 106.70(11), P(1)-C(1)-P(2) 130.29(15), Li(1)-C(1)-Li(2) 101.9(2), O(1)-Li(1)-C(1) 141.7(3), O(2)-Li(2)-C(1) 157.1(3).



Scheme 3 Mesomeric and isomeric (W and U) forms of L^{2-}.

Dissolving yellow crystals of $[\mathrm{LLi_2(THF)_3}]$ **5** and colourless crystals of $[\mathrm{LLi_2(THF)_2}]$ **6** in deuterated benzene afforded a yellow and a colourless solution, respectively, that provide very similar NMR characteristics. Both show one broadened doublet and one broadened septet for the isopropyl protons in ^{1}H NMR experiments and only one $^{7}\mathrm{Li}\{^{1}\mathrm{H}\}$ NMR resonance plus one broadened $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR resonance. These NMR characteristics can be expected from a flexible $(\mathrm{THF})_n\mathrm{Li}^+$ coordination in an overall solution structure deriving from the molecular structure found for **6**. In contrast, dissolving $[(\mathrm{LLi_2})_2]$ **2** in neat deuterated THF gives an intense yellow solution that again shows one very broadened doublet and one broadened septet in the ^{1}H NMR spectrum, one broad resonance in the $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR spectrum, but two resonances in the ^{7}Li NMR spectrum that support an overall structure comparable to that found for $[\mathrm{LLi_2(THF)_3}]$ **5** in the solid state. Upon cooling, ^{1}H NMR resonances for the isopropyl protons split to two resolved doublets and one septet and, as expected, no significant changes were observed to the $^{31}\mathrm{P}\{^{1}\mathrm{H}\}$ NMR resonance. A high THF concentration is likely needed to yield a dominating methandiide U-form in solution. A similar overall geometry may be expected when the compound is prepared in neat diethyl ether where it shows an orange-amber colour before work-up to a colourless compound (**4**).

Adding two equivalents of PMDTA (*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine) to a slurry of $[(\mathrm{LLi_2})_2]$ **2** in toluene eventually leads to the dissolution of the mixture and light yellow crystals of $[\mathrm{LLi_2(PMDTA)}]$ **7** could be obtained after work-up. The molecular structure of $[\mathrm{LLi_2(PMDTA)}]$ **7** (Fig. 5) shows it to have the methandiide fragment in the W-form constituting two spirocyclic four-membered rings with the lithium cations. The PMDTA coordination to those Li ions is asymmetric and one Li centre is chelated by two N atoms, the other Li centre is coordinated by the third N atom. This overall geometry is in contrast to the related TMEDA derivative **1** that derives from a U-form methandiide. At 60°C, $[\mathrm{LLi_2(PMDTA)}]$ **7** shows only one doublet and one septet for the isopropyl protons in solution, as found for the methandiide **4** and **6** for example. This is not unsurprising since the crystal structure of **7** almost shows a symmetric coordination arrangement and only one dative Li2-N4(···Li1) bond has to be broken and rapidly interchange or bridge between Li1 and Li2 to yield a symmetric species in solution.

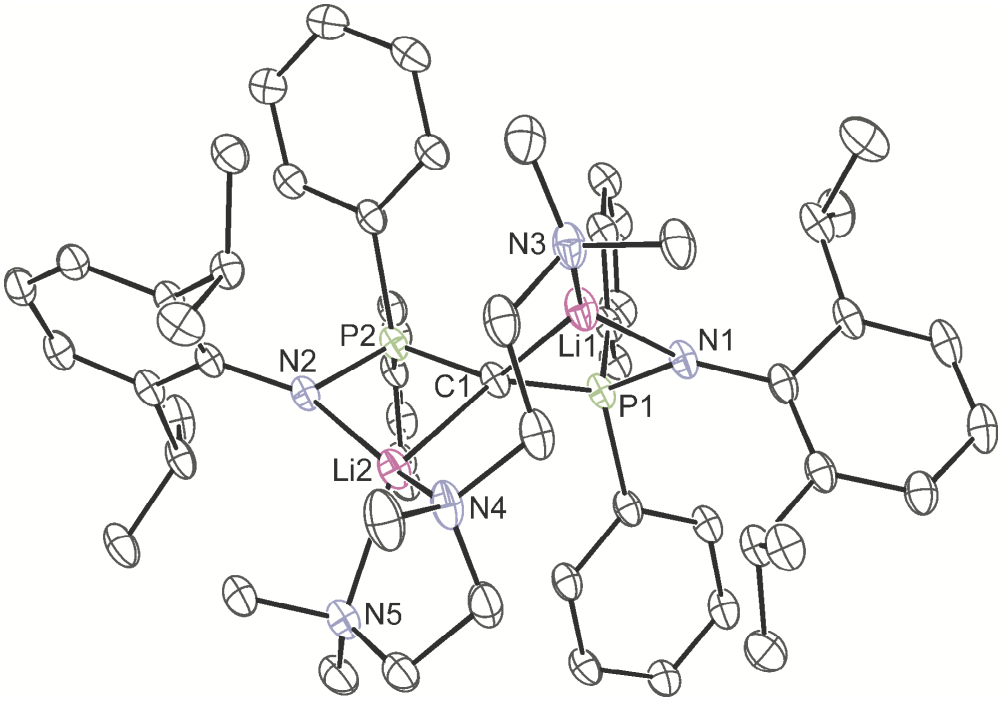
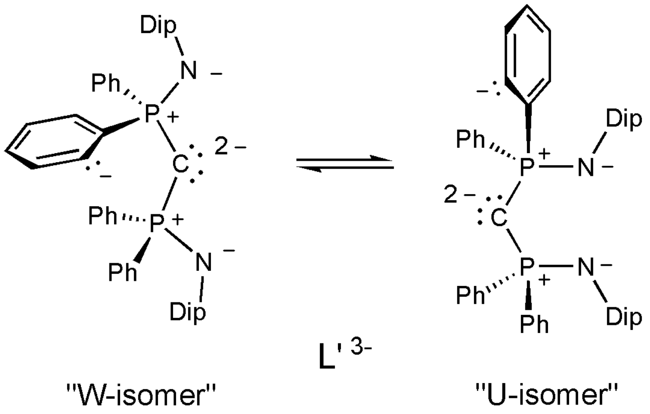


Fig. 5 Molecular structure of compound **7** (30% probability thermal ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)-N(1) 1.6266(14), P(2)-N(2) 1.6270(13), P(1)-C(1) 1.6973(15), C(1)-P(2) 1.6877(16), N(1)-Li(1) 1.928(3), C(1)-Li(1) 2.092(3), C(1)-Li(2) 2.224(3), Li(1)-N(3) 2.003(3), N(2)-Li(2) 1.998(3), Li(2)-N(4) 2.361(3), Li(2)-N(5) 2.142(3); P(2)-C(1)-P(1) 127.93(9), N(1)-P(1)-C(1) 106.27(7), N(2)-P(2)-C(1) 107.04(7), Li(1)-C(1)-Li(2) 101.50(12), N(1)-Li(1)-N(3) 136.48(15), N(2)-Li(2)-N(4) 145.38(15), N(2)-Li(2)-N(5) 109.70(13), N(5)-Li(2)-N(4) 81.33(11).

When slurries of [(LLi$_2$)$_2$] **2** in an aromatic solvent are treated with an additional equivalent of donor solvent-free alkyl lithium at elevated temperatures for a few hours, selective conversion to the new species [(L′Li$_3$)$_2$] **8** occurs, see scheme 1, with further deprotonation of one ortho-phenyl position per ligand, see scheme 4 for the modified ligand L′$^{3-}$.



Scheme 4 Isomeric (W and U) forms of L’$^{3-}$.

The reaction can be performed with *n*-butyllithium in hot toluene to give [(L′Li$_3$)$_2$] **8** in a crystallized yield of *ca.* 50%. The reaction can also be carried out in a sealed NMR tube in deuterated benzene starting either from H$_2$L, [HLLi] or [(LLi$_2$)$_2$] **2** with an excess of solid methyllithium at *ca.* 90°C and is remarkably clean by ^{31}P{^{1}H} NMR spectroscopy. Further selective deprotonation beyond L′$^{3-}$ using MeLi or *n*BuLi under more forcing conditions has not yet been achieved. Two solvates of complex **8** were structurally characterized, see Fig. 6 (and Fig. S3) for the molecular structure of **8**·3C$_6$H$_6$, and Fig. S2 for the structure of **8**·2C$_7$H$_8$, which both show a similar overall geometry. Compound **8** comprises a core of two W-form trianionic L′^{3}-ligands and six Li$^+$ cations. Each L′^{3}-ligand now contributes two N and two C donor atoms. One Li$^+$ centre (Li6) is coordinated by two N atoms and also has short contacts to the respective Dip ipso-carbon atoms, and the remaining five Li$^+$ ions are each three-coordinated in a slightly pyramidal manner either to three carbon atoms, or two carbon and one nitrogen, and can have long and weak contacts to aliphatic CH-groups. In **8**·3C$_6$H$_6$, the ortho-deprotonated phenyl groups show coordination to two (C52) or three (C3) Li centres.

Recrystallizing a sample of [(L′Li$_3$)$_2$] **8** from THF and *n*-hexane afforded yellow crystals of the monomeric THF-adduct [L′Li$_3$(THF)$_4$] **9** that were structurally characterised. Complex **9** crystallizes with two independent molecules in the asymmetric unit, both of which are shown in Fig. 7. Both molecules show a U-form methandiide unit with *N,N′*-chelated Li(THF) fragment, but the coordination of the Li$_2$(THF)$_3$ unit to the methandiide-phenyl anion chelate shows differences. The molecule depicted at the top of Fig. 7 contains a (THF)Li(μ-THF)Li(THF) moiety with one bridging THF ligand and a very short Li···Li distance of 2.294 Å, while the molecule depicted at the bottom only shows terminally bound THF ligands in (THF)$_2$Li···Li(THF) with a markedly longer Li···Li contact of 2.512(5) Å. The Li-C bonds in both molecules are in the expected range.

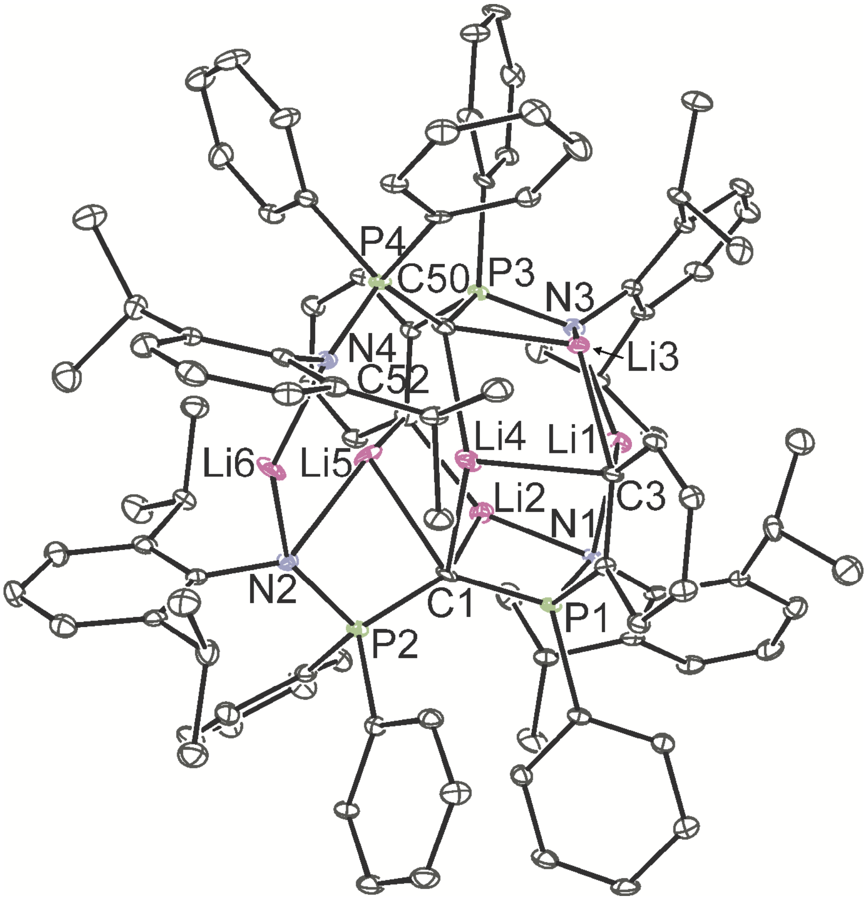


Fig. 6 Molecular structure of compound **8**·3C_6H_6 (30% probability thermal ellipsoids). Hydrogen atoms and solvent molecules have been omitted for clarity. The inorganic core of this molecule is depicted in Fig. S3. Selected bond lengths (Å) and angles (°): P(1)-N(1) 1.644(4), P(2)-N(2) 1.636(4), P(3)-N(3) 1.652(4), P(4)-N(4) 1.612(4), P(1)-C(1) 1.708(5), C(1)-P(2) 1.678(4), P(1)-C(8) 1.820(4), P(1)-C(2) 1.839(4), P(2)-C(14) 1.831(4), P(2)-C(20) 1.846(4), P(3)-C(51) 1.837(4), P(3)-C(57) 1.838(4), N(1)-Li(1) 1.980(8), P(3)-C(50) 1.708(4), P(4)-C(50) 1.681(4), N(1)-Li(2) 2.012(8), C(1)-Li(2) 2.220(9), C(1)-Li(4) 2.295(8), C(1)-Li(5) 2.302(8), Li(1)-N(3) 1.997(9), Li(1)-C(3) 2.367(9), N(2)-Li(6) 1.898(9), N(2)-Li(5) 2.475(9), Li(2)-C(52) 2.085(9), N(3)-Li(3) 2.045(8), C(3)-Li(3) 2.163(8), C(3)-Li(4) 2.231(9), Li(3)-C(50) 2.134(8), N(4)-Li(6) 1.889(8), Li(4)-C(50) 2.272(9), Li(5)-C(52) 2.174(9), Li(5)-C(50) 2.589(9), C(2)-C(3) 1.427(6), C(3)-C(4) 1.405(6), C(51)-C(52) 1.420(6), C(52)-C(53) 1.415(6); N(1)-P(1)-C(1) 107.5(2), Li(1)-N(1)-Li(2) 85.8(3), P(2)-C(1)-P(1) 131.2(3), Li(2)-C(1)-Li(4) 99.1(3), Li(2)-C(1)-Li(5) 67.4(3), Li(4)-C(1)-Li(5) 64.3(3), N(1)-Li(1)-N(3) 138.5(4), Li(6)-N(2)-Li(5) 85.0(3), Li(1)-N(3)-Li(3) 71.3(3), Li(3)-C(3)-Li(4) 70.0(3), Li(3)-C(3)-Li(1) 62.5(3), Li(4)-C(3)-Li(1) 89.2(3), N(4)-Li(6)-N(2) 137.9(5).

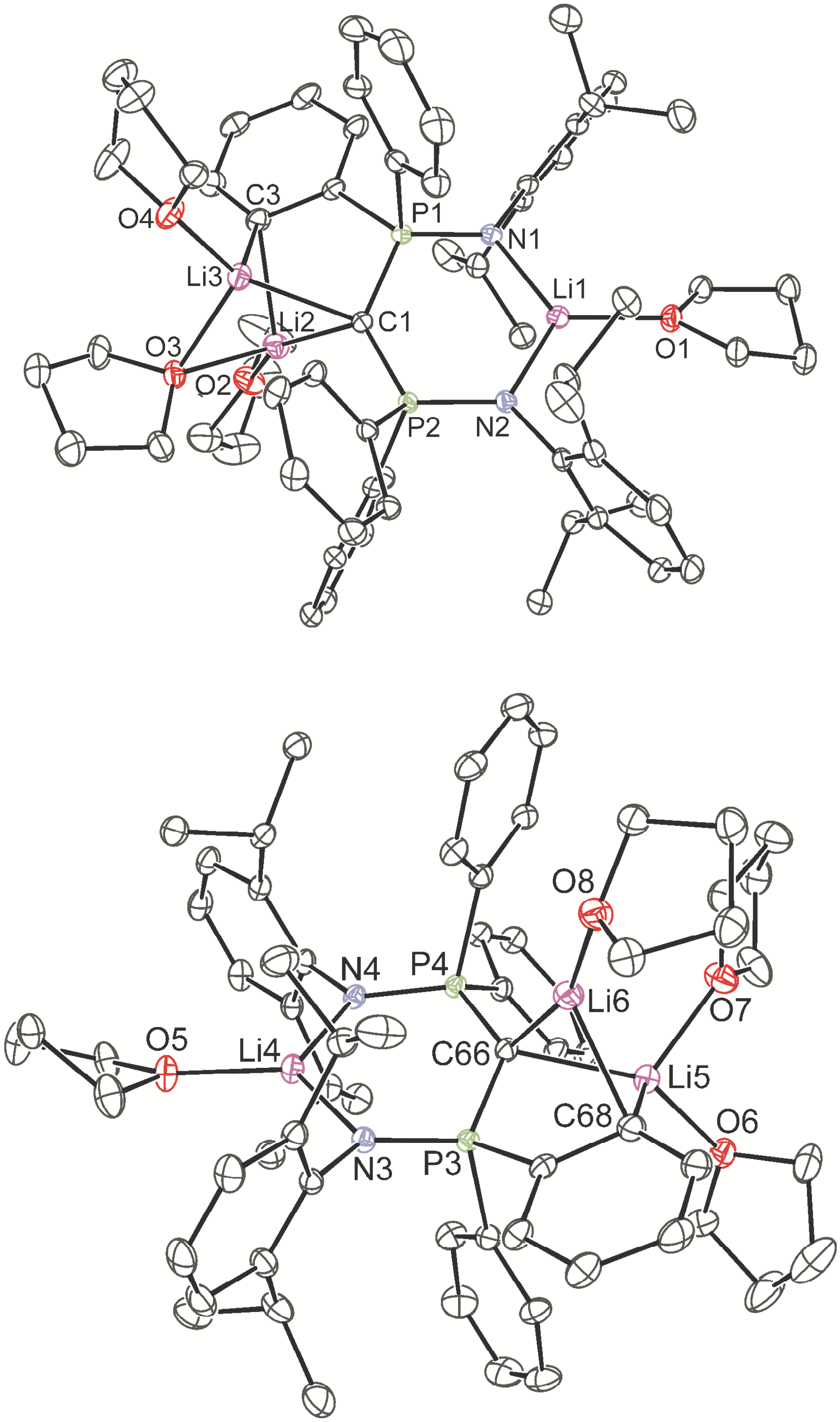
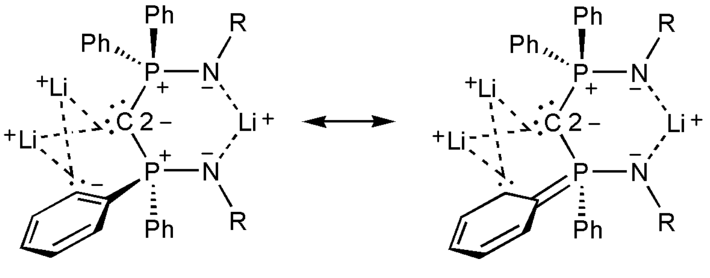


Fig. 7 Molecular structure of both crystallographically independent molecules of compound **9** (30% probability thermal ellipsoids); molecule 1 (top) and molecule 2 (bottom). Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): P(1)-N(1) 1.6179(15), P(2)-N(2) 1.6189(14), P(1)-C(1) 1.6849(17), C(1)-P(2) 1.6774(17), P(1)-C(2) 1.8390(17), P(1)-C(8) 1.8523(19), P(2)-C(20) 1.8470(17), P(2)-C(14) 1.8600(17), O(1)-Li(1) 1.956(3), N(1)-Li(1) 1.926(3), C(1)-Li(2) 2.193(4), C(1)-Li(3) 2.206(4), Li(1)-N(2) 1.919(3), Li(1)-C(38) 2.789(3),

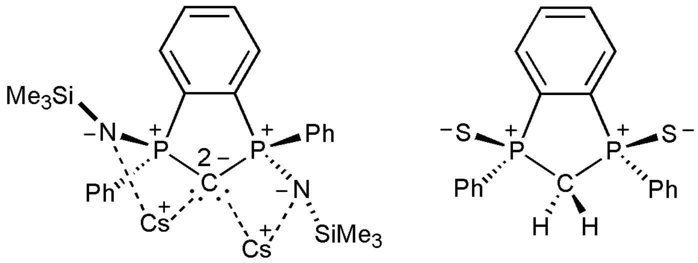
O(2)-Li(2) 1.951(4), Li(2)-O(3) 2.130(4), Li(2)-C(3) 2.222(4), Li(2)···Li(3) 2.294(5), C(2)-C(3) 1.417(3), C(3)-C(4) 1.417(2), P(3)-N(3) 1.6147(15), P(3)-N(3) 1.6147(15), P(3)-C(66) 1.6871(17), P(4)-C(66) 1.6782(17), P(3)-C(67) 1.8316(17), P(3)-C(73) 1.8564(18), P(4)-C(85), 1.8474(17), P(4)-C(79) 1.8500(18), O(3)-Li(3) 2.099(4), N(3)-Li(4) 1.924(3), C(3)-Li(3) 2.208(4), Li(3)-O(4) 1.983(4), P(4)-N(4) 1.6232(15), N(4)-Li(4) 1.923(3), Li(4)-O(5) 1.949(3), Li(4)-C(91) 2.753(3), Li(5)-O(7) 2.003(4), Li(5)-O(6) 2.042(6), Li(5)-C(66) 2.211(4), Li(5)-C(68) 2.224(4), Li(5)···Li(6) 2.512(5), Li(6)-O(8) 1.975(4), Li(6)-C(66) 2.174(4), Li(6)-C(68) 2.185(4), Li(6)···C(67) 2.588(4), C(67)-C(68) 1.424(3), C(2)-C(3) 1.413(3), N(1)-P(1)-C(1) 116.97(8); P(2)-C(1)-P(1) 127.97(10), Li(2)-C(1)-Li(3) 62.88(13), N(2)-Li(1)-N(1) 115.99(16), O(2)-Li(2)-O(3) 103.56(16), Li(3)-C(3)-Li(2) 62.39(13), O(4)-Li(3)-O(3) 108.90(16), N(4)-Li(4)-N(3) 115.11(15), O(7)-Li(5)-O(6) 89.57(19), C(66)-Li(6)-C(68) 87.75(14).

Compound **8** is significantly more soluble in aromatic hydrocarbons compared with compound **2**. The ^{1}H and ^{13}C{^{1}H} NMR spectra of [(L′Li$_3$)$_2$] **8** and [L′Li$_3$(THF)$_4$] **9**, the latter measured by dissolving **8** in deuterated THF to give an intense yellow solution, show the unsymmetrical nature of the complexes. For example, the ^{1}H NMR spectrum of [(L′Li$_3$)$_2$] **8** shows eight sharp doublets and four sharp septets for the protons of the isopropyl groups and according ^{13}C NMR resonances. The respective spectra in deuterated THF show partial broadening for some of the isopropyl resonances at various temperatures between 25 and 60°C. The ^{31}P{^{1}H} NMR spectrum of [(L′Li$_3$)$_2$] **8** in deuterated benzene shows two doublets with a $^{2}J_{PP}$ coupling constant of 55.3 Hz. In contrast, the same compound dissolved in deuterated THF with an expected molecular structure as that found in [L′Li$_3$(THF)$_4$] **9** having a planar U-form, only shows two relatively sharp singlets at room temperature that are somewhat broadened at 60°C, *i.e.* no significant coupling is observed likely due to the changes in the geometry of the PCP ligand fragment. The ^{7}Li{^{1}H} NMR spectrum of **8** shows only one broadened resonance, and two singlets with an approximate 2:1 ratio are observed in deuterated THF, as can be expected from the solid state structure of **9**. Of note is a downfield resonances in the ^{13}C{^{1}H} NMR spectrum of [L′Li$_3$(THF)$_4$] **9** that shows a significantly broadened doublet of *ca.* 48 Hz (J_{PC}), that likely represents a poorly resolved doublet of a doublet, with a chemical shift of 194.4 ppm. No significant changes in the chemical shift, coupling constant or signal broadening of this resonance have been found with changes to temperature or NMR spectrometer field strength. Additional HSQC and HMBC NMR experiments show no directly attached hydrogen atom, but indicate longer range couplings to phenyl-H, and point towards the assignment of the lithiated ortho-phenyl position in **9**. Compound **8** also shows one somewhat downfield shifted doublet of a doublet at 160.2 ppm in its ^{13}C{^{1}H} NMR spectrum. The chemical shift of 194.4 ppm in **9** is reminiscent of s-block metal carbene complexes[4] and raises the question whether a partial description as a Li-carbene complex is warranted, see scheme 5. Inspecting the bond lengths in the lithiated part of **9**, and comparable distances in **8**, suggests a slight bond lengthening of the aromatic C-C bonds on the deprotonated carbon atom by approximately 0.02 Å, which may be just significant enough, though no concomitant significant shortening of the P-C_{phenyl} bonds is observed. These small changes may point to a minor participation of resonance form **B**.



Scheme 5 Simplified aryllithium (**A**) and carbene-phosphorane (**B**) descriptions of [L′Li_3]-fragments

Metallation in the ortho-position of the P-bound phenyl group as observed in **8** and **9** has previously been found for related ligand systems, albeit structurally characterized compounds are mainly known with late transition metals coordinated to a methanide ligand.[5] Some of these examples also feature downfield ^{13}C NMR resonances (*c.f.* **9**) for the metallated phenyl position, such as 177.8 ppm (Rh-C_{aryl})[5c] and 172-175 ppm (Ru-C_{aryl}).[5d] Metallation in this ortho-phenyl position with highly electropositive metal ions has indirectly been observed for caesium.[2e] The attempt to isolate a dicaesium methandiide complex led to ring formation via ortho-phenyl metallation, and presumable PhCs elimination, and afforded the remarkable red methandiide complex **10** (see scheme 6 for a simplified representation) after storing the sample for a prolonged time. A similar metallation step is used to induce ring formation to a potassium methanide complex that can be hydrolyzed to the respective methane derivative **11**, see scheme 6, which has been employed in the synthesis of methandiide main group complexes.[6]



Scheme 6 Compounds **10** (simplified) and **11**.

Conclusions

We have presented convenient syntheses to a range of di- and tri-lithiated complexes of a sterically demanding bis(iminophosphoranyl)methandiide with and without donor molecules. Various molecular structures with W and U shape methandiide isomeric forms have been found and their interconversions are likely low energy processes. In general, the species show flexible coordination in solution and the U isomeric form appears to be dominant in neat coordinating solvents such as THF. Access to a stable trianionic methandiide with selective ortho-lithiation of a P-bound phenyl group has been reported for the first time. The lithium complexes of L^{2-} and L'^{3-} represent suitable precursors for salt metathesis reactions, as has already been demonstrated by the recent synthesis of heavier group 15 complexes of L^{2-}.[7]

Experimental section

General considerations

All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of high purity dinitrogen. Benzene, toluene, tetrahydrofurane and hexane were dried and distilled over molten potassium; Et_2O was dried and distilled from Na/K alloy. ^1H, $^7Li\{^1H\}$, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker DPX 300, Bruker Avance 400 or Bruker AVII+ 500 spectrometer in deuterated benzene and were referenced to the residual ^1H or $^{13}C\{^1H\}$ resonances of the solvent used, or external aqueous LiCl, or H_3PO_4 solutions, respectively. IR spectra were recorded using a Perkin Elmer RXI FT-IR spectrometer as Nujol mulls between NaCl plates, or on solids protected with a thin layer of nujol using an Agilent Cary 630 ATR FTIR spectrometer. Melting points were determined in sealed glass capillaries under dinitrogen and are uncorrected. Elemental analyses were performed by the Elemental Analysis Service at London Metropolitan University. H_2L was prepared according to a literature procedure.[8] All other reagents were used as received from commercial sources. Solid MeLi was obtained by removing all volatiles from a commercially available solution in diethylether. Abbreviations: br = broad, vbr = very broad, m = multiplet. No $^{13}C\{^1H\}$ NMR resonance on any alkali metal methandiide carbon atom was observed despite long acquisition times, as found in previous studies.[1,2] NMR scale reactions were typically carried out on *ca.* 20 mg samples in 5 mm NMR tubes with J.Young stopcock in dried deuterated benzene or THF (*ca.* 0.55 mL), followed by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy, and are described in the main text.

[{LLi$_2$}$_2$] 2

*n*BuLi (3.48 mL of a 1.6 M solution in hexanes, 5.57 mmol, 2.04 equiv) was slowly added over 15 min to a cooled (*ca.* 8°C) solution of H$_2$L (2.0 g, 2.72 mmol, 1.0 equiv.) in benzene (50 mL). The reaction mixture was stirred at this temperature for approximately 4 h, and then stirred another 20 h at room temperature. The formed white crystalline precipitate was filtered off, and the solution was stored at 6°C for two weeks yielding more crystalline material. The obtained solids were dried under vacuum at 40 °C. A ^{1}H and ^{31}P{^{1}H} NMR spectrum of an aliquot of the supernatant solution showed it to contain mainly [HLLi] and [{LLi$_2$}$_2$] **2**. Crystals of [{LLi$_2$}$_2$] **2**·4 C_6H_6 and/or [{LLi$_2$}$_2$] **2**·5 C_6H_6 and [{LLi$_2$}$_2$] **2**·2 C_7H_8 can be obtained by recrystallizing samples from warm benzene or toluene, respectively. Once crystallised, the solvates of [{LLi$_2$}$_2$] **2** only show a very poor solubility in aromatic solvents even at elevated temperatures and no meaningful NMR data could be acquired in those solvents. ^{7}Li{^{1}H} and ^{13}C{^{1}H} NMR data was recorded in (or with the help of) donor solvents; please refer to donor adducts of [{LLi$_2$}$_2$], *e.g.* compound **5**. Yield: 1.07 g of **2**·n C_6H_6 (n ≈ 2) (47%); Mp.: 265-270°C: melts with some decomposition to an amber-yellow liquid; ^{1}H NMR (C_6D_6, 300.1 MHz, 338 K): δ 0.11 (d, br, $J \approx 6.7$ Hz, 12H, CH(C*H*$_3$)$_2$), 0.13 (d, br, $J \approx 6.7$ Hz, 12H, CH(C*H*$_3$)$_2$), 0.62 (d, br, $J \approx 6.7$ Hz, 12H, CH(C*H*$_3$)$_2$), 1.55 (d, br, $J \approx 6.7$ Hz, 12H, CH(C*H*$_3$)$_2$), 3.18 (sept, br, 4H, C*H*(CH$_3$)$_2$), 3.89 (br, 4H, C*H*(CH$_3$)$_2$), 6.56-8.18 (br m, 52H, Ar-*H*); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 338 K): δ 22.0 (s, br); IR (nujol), ν~/cm^{-1}: 1587w, 1459s, 1433m, 1377m, 1347m, 1303m, 1259m, 1235m, 1143s, 1125s, 1105s, 1035m, 1026m, 941m, 815m, 780s, 754m, 736s, 699m, 675m; elemental analysis (%) for $C_{98}H_{108}Li_4N_4P_4$ (1493.59 g·mol^{-1}, vacuum dried sample): calcd: C 78.81, H 7.29, N 3.75; found: C 78.62, H 7.58, N 3.72.

[HC(Ph$_2$PNDip)(Ph$_2$P)Li(THF)$_2$] 3

A significantly lower and more variable yield of [{LLi$_2$}$_2$] **2** was obtained when the lithiation of H$_2$L with 2.3 equiv. of *n*BuLi was carried out in toluene at various temperatures. The supernatant solution contained a mixture of compounds including [HLLi], [{LLi$_2$}$_2$] **2**, [{L′Li$_3$}$_2$] **8** and other products in varying ratios according to ^{1}H and ^{31}P{^{1}H} NMR spectroscopy. Removal of all volatiles from the supernatant solution, subsequent extraction into hexane and removal of all volatiles afforded in one case a product mixture with two dominating broad doublets (-22.3 ppm, 25.1 ppm, J_{PP} = 103 Hz) in its ^{31}P{^{1}H} NMR spectrum. Recrystallisation of this material from hexane/THF (5:1, room temperature to -30°C) afforded [HC(Ph$_2$PNDip)(Ph$_2$P)Li(THF)$_2$] **3** as colourless crystals. Spectroscopic data for **3**: Mp.: above 128°C softer, and eventually fully melts up to *ca*. 160°C and shows decomposition at higher temperatures. ^{1}H NMR (C_6D_6, 300.1 MHz, 303 K): δ 0.92 (d, J =

6.9 Hz, 12H, $\mathrm{CH(C}H_3)_2$), 1.23 ($\mathrm{m_c}$, 8H, THF-$\mathrm{OCH_2C}H_2$), 1.64 (dd, $J_{\mathrm{PH,PH}}$ = 14.4, 6.9 Hz, 1H, CH), 3.33 ($\mathrm{m_c}$, 8H, THF-$\mathrm{OC}H_2$), 3.85 (sept, J = 6.9 Hz, 2H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 6.92-7.23 (m, 15H, Ar-*H*), 7.64-8.00 (m, 8H, Ar-*H*); ^{7}Li NMR ($\mathrm{C_6D_6}$, 155.5 MHz, 300 K): δ 1.37 (d, $J_{\mathrm{P^7Li}}$ = 39 Hz); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 75.5 MHz, 303 K): δ 17.5 (d, br, J_{PC} = 148 Hz, $\mathrm{P_2}C\mathrm{H}$), 24.4 ($\mathrm{CH(}C\mathrm{H_3)_2}$), 25.5 (THF-$\mathrm{OCH_2}C\mathrm{H_2}$), 28.0 ($C\mathrm{H(CH_3)_2}$), 68.3 (THF-$\mathrm{O}C\mathrm{H_2CH_2}$), 121.1 (d, J_{PC} = 3.7 Hz, Ar-*C*), 123.5 (d, J_{PC} = 3.1 Hz, Ar-*C*), 127.0 (Ar-*C*), 127.5 (d, J_{PC} = 10.7 Hz, Ar-*C*), 128.2 (Ar-*C*, partially hidden by the solvent resonances), 129.3 (d, J_{PC} = 2.6 Hz, Ar-*C*), 132.4 (d, J_{PC} = 17.3 Hz, Ar-*C*), 132.6 (d, J_{PC} = 8.6 Hz, Ar-*C*), 140.9 (dd, $J_{\mathrm{PC,PC}}$ = 98.3, 2.1 Hz, Ar-*C*), 145.2 (d, J_{PC} = 6.3 Hz, Ar-*C*), 147.0 (d, J_{PC} = 8.4 Hz, Ar-*C*), 148.0 (d, J_{PC} = 8.2 Hz, Ar-*C*); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 121.5 MHz, 303 K): δ -21.1 (dq, J_{PP} = 117Hz, $J_{\mathrm{P^7Li}}$ = 39 Hz), 24.0 (d, J_{PP} = 117 Hz); IR (nujol), ν~/cm^{-1}: 1584m, 1462s, 1434s, 1377s, 1356m, 1320m, 1259s, 1208m, 1158m, 1106m, 1158s, 1045s, 1029m, 1005m, 971m, 939m, 890m, 815m, 770s, 754m, 737s, 696s.

[$\mathbf{LLi_2(OEt_2)_2}$] 4

MeLi (1.4 mL of a 1.6 M solution in diethylether, 2.24 mmol, 3.2 equiv) was added to a cooled (-70°C) solution of $\mathrm{H_2L}$ (0.51 g, 0.694 mmol, 1.0 equiv.) in $\mathrm{Et_2O}$ (25 mL), the mixture was warmed to room temperature (orange-amber) and stirred for two days. Benzene (15 mL) was added, the majority of the solvent was removed under reduced pressure, and hexane (10 mL) was added to the residue. The product started to crystallise, the mixture was stored at 5°C until crystallisation finished, the product was filtered off and dried under vacuum to afford colourless [$\mathrm{LLi_2(OEt_2)_2}$] **4**. An X-ray crystal structure of **4** was of very poor quality, and is thus not included here, but shows both the compound composition and its W-isomer geometry, see main text. Yield: 0.40 g (64%). Mp.: 168-173°C decomposition; turns yellow, plus gas formation; ^{1}H NMR ($\mathrm{C_6D_6}$, 400.2 MHz, 294 K): δ 0.81 (br, 24H, $\mathrm{CH(C}H_3)_2$), 1.14 (t, J = 7.0 Hz, 12H, $\mathrm{OCH_2C}H_3$), 3.39 (q, br, 8H, $\mathrm{OC}H_2\mathrm{CH_3}$), 3.64 (br, 4H, $\mathrm{C}H\mathrm{(CH_3)_2}$), 6.68-7.76 (m, 26H, Ar-*H*); ^{7}Li NMR ($\mathrm{C_6D_6}$, 155.5 MHz, 300 K): δ 2.73 (s); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 100.6 MHz, 294 K): δ 14.9 ($\mathrm{OCH_2}C\mathrm{H_3}$), 24.2 (br, $\mathrm{CH(}C\mathrm{H_3)_2}$), 28.3 ($C\mathrm{H(CH_3)_2}$), 119.9 (Ar-*C*), 123.0 (br, Ar-*C*), 126.5 (vtr, J_{PC} = 4.8 Hz, Ar-*C*), 127.4 (br, partially hidden by the solvent resonance, Ar-*C*), 132.1 (br, Ar-*C*), *ca.* 140 (vbr, broadened into the baseline, Ar-*C*), 144.7 (vtr, J_{PC} = 3.3 Hz, Ar-*C*), 148.3 (Ar-*C*); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR ($\mathrm{C_6D_6}$, 121.5 MHz, 333 K): δ 14.7 (s, br); IR (nujol), ν~/cm^{-1}: 1586m, 1465s, 1429s, 1389s, 1366s, 1324s, 1315s, 1262s, 1231m, 1210m, 1177m, 1139s, 1099s, 1065m, 1026m, 999m, 973s, 930m, 810m, 768s, 740s, 702s, 691s, 660m.

[LLi$_2$(THF)$_3$] 5 and [LLi$_2$(THF)$_2$] 6

MeLi (3.3 mL of a 1.6 M solution in diethylether, 5.28 mmol, 3.9 equiv) was added to a cooled (-40°C) solution of H$_2$L (1.00 g, 1.36 mmol, 1.0 equiv.) in Et$_2$O (25 mL), the orange mixture was warmed to room temperature and stirred for two days. THF (4 mL) was added, stirred for one hour and all volatiles were removed. The residue was extracted with an *n*-hexane (9 mL) and THF (9 mL) mixture, filtered and cooled to -30°C to afford yellow crystals of [LLi$_2$(THF)$_3$] **5**. Concentration of the supernatant solution to *ca.* 10 mL and cooling to -30°C again afforded another small crop of **5**. Further concentration to *ca.* 4 mL and cooling to -30°C again afforded a crystalline mixture of yellow [LLi$_2$(THF)$_3$] **5** and colourless [LLi$_2$(THF)$_2$] **6**. Yield for **5**: 0.90 g (69%). Colourless **6** was further obtained by prolonged pumping on **5**, dissolving in a small amount of toluene, concentrating and storing at -30°C to afford colourless crystals of [LLi$_2$(THF)$_2$] **6**. Alternatively, a small quantity of [{LLi$_2$}$_2$] **2** was dissolved in a minimal amount of THF to give an intense yellow solution. Addition of some *n*-hexane and cooling afforded some crystals of yellow [LLi$_2$(THF)$_3$] **5**.

Data for [LLi$_2$(THF)$_3$] **5**: Mp.: starts to lose yellow colour above *ca.* 120°C; 208-212°C: full decomposition towards red-brown. Isolated crystals dissolved in deuterated benzene to give a yellow solution: ^{1}H NMR (C$_6$D$_6$, 400.2 MHz, 300 K): δ 0.95 (br, 24H, CH(C*H*$_3$)$_2$), 1.38 (br, 12H, THF-OCH$_2$C*H*$_2$), 3.61 (br, 12H, THF-OC*H*$_2$), 3.79 (sept, br, 4H, C*H*(CH$_3$)$_2$), 6.79-7.14 (m, 18H, Ar-*H*), 7.49 (br, 8H, Ar-*H*); ^{7}Li NMR (C$_6$D$_6$, 155.5 MHz, 300 K): δ 2.76 (s, br); ^{13}C{^{1}H} NMR (C$_6$D$_6$, 100.6 MHz, 300 K): δ 23.8 (CH(*C*H$_3$)$_2$), 25.3 (THF-OCH$_2$*C*H$_2$), 28.3 (*C*H(CH$_3$)$_2$), 68.1 (THF-O*C*H$_2$), 119.7 (vtr, not resolved, Ar-*C*), 122.9 (Ar-*C*), 126.5 (vtr, J_{PC} = 4.9 Hz, Ar-*C*), 127.5 (Ar-*C*, partially hidden by the solvent resonance), 131.8 (vtr, not resolved, Ar-*C*), *ca.* 141 (br, weak, Ar-*C*), 144.4 (vtr, J_{PC} = 3.4 Hz, Ar-*C*), 149.1 (Ar-*C*); ^{31}P{^{1}H} NMR (C$_6$D$_6$, 162.0 MHz, 300 K): δ 11.6 (s, br); NMR data for compound [{LLi$_2$}$_2$] **2** dissolved in neat THF-d$_8$ to give an intense yellow solution: ^{1}H NMR (C$_4$D$_8$O, 500.1 MHz, 298 K): δ 0.68 (vbr, 24H, CH(C*H*$_3$)$_2$), 3.88 (br, 4H, C*H*(CH$_3$)$_2$), 6.53 (t, *J* = 7.5 Hz, 2 H, Ph-*H*), 6.70 (d, *J* = 7.5 Hz, 4 H, Ph-*H*), 7.06 (br, 12H, Ar-*H*), 7.59 (br, 8H, Ar-*H*); ^{1}H NMR (C$_4$D$_8$O, 500.1 MHz, 232 K): δ 0.41 (br, 12H, CH(C*H*$_3$)$_2$), 1.02 (br, 12H, CH(C*H*$_3$)$_2$), 3.92 (sept, *J* = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 6.52 (t, *J* = 7.5 Hz, 2H, Ph-*H*), 6.68 (d, *J* = 7.5 Hz, 4H, Ph-*H*), 7.09 (br, 12H, Ar-*H*), 7.58 (br, 8H, Ar-*H*); ^{7}Li NMR (C$_4$D$_8$O, 194.4 MHz, 298 K): δ 1.52 (s, br), 0.62 (s, br); ^{13}C{^{1}H} NMR (C$_4$D$_8$O, 125.8 MHz, 299 K): δ 24.7 (vbr, CH(*C*H$_3$)$_2$), 28.6 (*C*H(CH$_3$)$_2$), 119.6 (Ar-*C*), 123.3 (Ar-*C*), 127.1 (vtr, J_{PC} = 5.1 Hz, Ar-*C*), 127.6 (Ar-*C*), 132.9 (vtr, J_{PC} = 4.1 Hz, Ar-*C*), 145.5 (Ar-*C*), *ca.* 146-148 (vbr, Ar-*C*), 151.5 (br, Ar-*C*); ^{31}P{^{1}H} NMR (C$_4$D$_8$O, 202.5 MHz, 298 K): δ 7.6 (s, br); Note: no significant changes to the ^{31}P{^{1}H} NMR spectrum were observed upon cooling and only minor sharpening of the resonance was found. IR (nujol), ν~/cm^{-1}: 1584m, 1462s, 1433s, 1388m, 1377m, 1366m, 1327m, 1261m, 1230s, 1178m, 1158m, 1105m, 1071m, 1045m, 1983m, 914m, 890m, 793m, 764m, 746m, 730m, 698s, 665m; elemental analysis (%) for $C_{61}H_{78}Li_2N_2O_3P_2$ (963.11 g·mol^{-1}): calcd: C 76.07, H 8.16, N 2.91; found: C 75.45, H 8.22, N 3.01.

Data For [$LLi_2(THF)_2$] **6**: Mp.: *ca.* 210°C: softer, 215-220°C: decomposition to a red-brown oil. Isolated crystals dissolved in deuterated benzene to give a colourless solution. The NMR spectra are very similar to those of yellow [$LLi_2(THF)_3$] **5** dissolved in deuterated benzene: ^{1}H NMR (C_6D_6, 400.2 MHz, 300 K): δ 0.95 (br, 24H, CH(C*H*$_3$)$_2$), 1.33 (br, 8H, THF-OCH$_2$C*H*$_2$), 3.63 (br, 8H, THF-OC*H*$_2$), 3.77 (sept, br, 4H, C*H*(CH$_3$)$_2$), 6.82-7.15 (m, 18H, Ar-*H*), 7.47 (br, 8H, Ar-*H*); ^{7}Li NMR (C_6D_6, 155.5 MHz, 300 K): δ 2.85 (s, br); ^{13}C{^{1}H} NMR (C_6D_6, 75.5MHz, 300 K): δ 24.0 (CH(*C*H$_3$)$_2$), 25.5 (THF-OCH$_2$*C*H$_2$), 28.6 (*C*H(CH$_3$)$_2$), 69.0 (THF-O*C*H$_2$), 119.9 (vtr, not resolved, Ar-*C*), 123.1 (Ar-*C*), 126.7 (vtr, J_{PC} = 5.0 Hz, Ar-*C*), 127.6 (Ar-*C*, partially hidden by the solvent resonance), 132.1 (vtr, J_{PC} = 3.7 Hz, Ar-*C*), 141.6 (vtr, br, weak, J_{PC} = 38.1 Hz, Ar-*C*), 144.6 (vtr, J_{PC} = 3.6 Hz, Ar-*C*), 148.7 (vtr, not resolved, Ar-*C*); ^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz, 300 K): δ 11.8 (s, br).

[LLi_2(PMDTA)] 7

Dry PMDTA (*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine, *ca.* 91 µL, 76.6 mg, 0.442 mmol, 2.2 eq) was added to a suspension of [{LLi_2}$_2$] **2** (0.30 g, 0.20 mmol, 1.0 equiv) in toluene (15 mL) at room temperature. The mixture was vigorously stirred for one hour to give a light yellow solution. All volatiles were removed under vacuum to give an oily residue (that can start to solidify upon standing) and subsequently, *n*-hexane (20 mL) was added, the mixture was vigorously stirred for 30 min and formed a light-yellow crystalline precipitate. The product was filtered off and dried under vacuum. Crystals suitable for X-ray diffraction were grown from *n*-hexane/toluene at -30°C. Yield: 0.30 g (81%); Mp: 180-185°C, melts to yellow liquid; darkens via brown-orange to dark red-brown at higher temperatures. The ^{1}H NMR spectrum at 25°C shows some broadened resonances that sharpen at higher temperature; data given at 60°C: ^{1}H NMR (C_6D_6, 300.1 MHz, 333 K): δ 0.82 (d, *J* = 6.9 Hz, 24H, CH(C*H*$_3$)$_2$), 2.06 (s, br, 3H, PMDTA-NC*H*$_3$), 2.21 (s, br, 12H, PMDTA-N(C*H*$_3$)$_2$), 2.29 and 2.39 (2 broad overlapping m, 8H, PMDTA-C*H*$_2$), 3.77 (sept, *J* = 6.9 Hz, 4H, C*H*(CH$_3$)$_2$), 6.81-7.09 (m, 18H, Ar-*H*), 7.42 (vbr, 8H, Ar-*H*); ^{7}Li NMR (C_6D_6, 155.5 MHz, 300 K): δ 2.6 (m); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 333 K): δ 24.9 (CH(*C*H$_3$)$_2$), 28.3 (*C*H(CH$_3$)$_2$), 42.7 (PMDTA-N*C*H$_3$), 46.6 (PMDTA-N(*C*H$_3$)$_2$), 58.4 (2 ×, PMDTA-*C*H$_2$), 120.1 (vtr, not resolved, Ar-*C*), 123.3 (Ar-*C*), 126.4 (vtr, J_{PC} = 10.7 Hz, Ar-*C*), 127.6 (Ar-*C*), 133.3 (vtr, J_{PC} = 3.9 Hz, Ar-*C*), 141.5 (vtr, br, weak, J_{PC} = 36.7 Hz, Ar-*C*), 145.0 (vtr, J_{PC} = 3.5 Hz, Ar-*C*), 148.7 (Ar-*C*);

$^{31}P\{^1H\}$ NMR (C_6D_6, 121.5 MHz, 333 K): δ 14.2 (s, br); IR (solid), ν~/cm^{-1}: 1586w, 1453s, 1432s, 1380m, 1342s, 1286m, 1256m, 1233m, 1220m, 1180m, 1146m, 1108s, 1053m, 1026m, 999m, 931m, 780m, 753m, 734s, 720m, 690s.

[{L′Li$_3$}$_2$] 8 and [L′Li$_3$(THF)$_4$] 9

Method A: *n*BuLi (2.67 mL of a 1.6 M solution in hexanes, 4.27 mmol, 3.3 equiv) was added to a cooled (10°C) solution of H_2L (0.95 g, 1.29 mmol, 1.0 equiv.) in toluene (15 mL). The reaction mixture was stirred at room temperature for approximately 2 h, slowly brought to the boil and refluxed for 2 h. The mixture was concentrated to *ca.* 10 mL and cooled to 5°C to afford colourless crystals of [{L′Li$_3$}$_2$] **8**·2 C_7H_8. The supernatant solution was concentrated to *ca.* 4 mL and cooled again to afford a second crop of [{L′Li$_3$}$_2$] **8**·2 C_7H_8. Crystals of [{L′Li$_3$}$_2$] **8**·3 C_6H_6 were obtained by recrystallising a sample from warm benzene. Yield of [{L′Li$_3$}$_2$] **8**·2 C_7H_8: 0.55 g (50%).

Method B: [{L′Li$_3$}$_2$] **8** can be obtained by heating [{LLi$_2$}$_2$] **2** (*ca.* 15 mg) with an excess (more than two equivalents) of solid MeLi (*ca.* 4 mg) in a sealed NMR tube with J. Young cap to 90-95°C for 3-5 hours in deuterated benzene (*ca.* 0.55 mL). Alternatively, this reaction can be performed starting from H_2L or [HLLi][2c] and an excess of solid MeLi under the same conditions, and provides a material that is essentially clean by $^{31}P\{^1H\}$ NMR spectroscopy. Excess polymeric MeLi remains as an insoluble solid at the end of the reaction.

Crystals of [L′Li$_3$(THF)$_4$] **9** were obtained by dissolving a small amount of [{L′Li$_3$}$_2$] **8** in THF, concentrating, adding *n*-hexane and storing at 5°C to afford some colourless to light yellow crystals.

Data for [{L′Li$_3$}$_2$] **8**: Mp.: above *ca.* 250°C colour change towards off-white, above *ca.* 260°C towards beige, and *ca.* 268°C towards red-brown. ^1H NMR (C_6D_6, 400.2 MHz, 300 K): δ -0.19 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.21 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.44 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.50 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.62 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.66 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 0.74 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 1.82 (d, J = 6.8 Hz, 6H, CH(CH_3)$_2$), 2.72 (sept, J = 6.8 Hz, 2H, CH(CH_3)$_2$), 2.89 (sept, J = 6.8 Hz, 2H, CH(CH_3)$_2$), 3.45 (sept, J = 6.8 Hz, 2H, CH(CH_3)$_2$), 3.79 (sept, J = 6.8 Hz, 2H, CH(CH_3)$_2$), 6.36-7.42 (m, 42H, Ar-*H*), 7.56-7.68 (m, 2H, Ar-*H*), 7.90 (br, 4H, Ar-*H*), 8.72 (d, J = 6.4 Hz, 2H, Ph-*H*); ^7Li NMR (C_6D_6, 155.5 MHz, 300 K): δ 4.3 (br); $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz, 313 K): δ 20.7, 22.9, 23.8, 24.3, 25.0, 25.6, 27.1, 27.7, 28.5, 29.4, 29.7, 30.2 (8 × CH(CH$_3$)$_2$, 4 × CH(CH$_3$)$_2$), 122.5 (d, J_{PC} = 3.9 Hz, Ar-*C*), 123.1 (d, J_{PC} = 2.9 Hz, Ar-*C*), 123.4 (Ar-*C*), 123.9 (d, J_{PC} = 3.8 Hz, Ar-*C*), 124.3 (d, J_{PC} = 3.4 Hz, Ar-*C*), 124.6 (Ar-*C*), 124.7-124.9 (m, Ar-*C*), 125.4 (Ar-*C*), 126.3-126.5 (m, Ar-*C*), 127.3 (d, J_{PC} = 9.9 Hz, Ar-*C*), *ca.* 128 some resonance(s) likely hidden by the strong signal, 128.8-129.2 (m, Ar-*C*), 129.8-130.0 (m, Ar-*C*), 130.7 (d, not resolved, Ar-*C*), 131.0 (Ar-*C*), 132.6 (d, J_{PC} = 6.9 Hz, Ar-*C*), 133.6 (d, J_{PC}

= 6.7 Hz, Ar-*C*), 134.9 (d, J_{PC} = 8.5 Hz, Ar-*C*), 137.0 (d, J_{PC} = 86.1 Hz, Ar-*C*), 138.8 (d, br, weak, J_{PC} = 94.9 Hz, Ar-*C*), 142.4 (Ar-*C*), 142.8 (Ar-*C*), 143.1 (Ar-*C*), 143.4 (Ar-*C*), 144.8 (d, J_{PC} = 6.3 Hz, Ar-*C*), 145.7 (d, J_{PC} = 5.3 Hz, Ar-*C*), 146.2 (d, J_{PC} = 5.9 Hz, Ar-*C*), 147.7-148.0 (m, Ar-*C*), 148.8 (d, J_{PC} = 6.4 Hz, Ar-*C*), 160.2 (dd, $J_{PC,PC}$ = 110.2, 1.5 Hz, Ar-*C*); ^{31}P{^{1}H} NMR (C_6D_6, 162.0 MHz, 300 K): δ 18.6 (d, J_{PP} = 55.3 Hz), 32.8 (d, J_{PP} = 55.3 Hz); IR (nujol), ν~/cm^{-1}: 1588w, 1461s, 1433m, 1377s, 1308m, 1260m, 1186m, 1137m, 1096s, 1039m, 1026m, 962m, 940m, 812m, 801m, 778s, 729s, 697s, 654m; elemental analysis (%) for $C_{98}H_{106}Li_6N_4P_4$ (1505.46 g·mol^{-1}, vacuum dried sample): calcd: C 78.19, H 7.10, N 3.72; found: C 77.99, H 7.02, N 3.61.

NMR data for [L′Li$_3$(THF)$_4$] **9** was obtained by dissolving [{L′Li$_3$}$_2$] **8** in deuterated THF to give a yellow solution. Note: some NMR spectra are given at different and various temperatures. Some minor merging and sharpening of resonances has been observed across the investigated temperature range. ^{1}H NMR (THF-d$_8$, 400.2 MHz, 300 K): δ *ca.* 0.2-1.0 (vbr, 12H, CH(C*H*$_3$)$_2$), 0.48 (d, br, 3H, CH(C*H*$_3$)$_2$), 0.66 (d, br, 3H, CH(C*H*$_3$)$_2$), 0.80 (d, br, 3H, CH(C*H*$_3$)$_2$), 1.30 (d, br, 3H, CH(C*H*$_3$)$_2$), 3.33 (sept, br, 1H, C*H*(CH$_3$)$_2$), 3.63 (sept, br, 2H, C*H*(CH$_3$)$_2$), 4.22 (sept, br, 1H, C*H*(CH$_3$)$_2$), 6.52-7.57 (m, 20H, Ar-*H*), 7.48 (t, *J* = 8.4 Hz, 2H, Ar-*H*), 7.68 (t, *J* = 8.4 Hz, 2H, Ar-*H*), 7.93 (d, *J* = 6.4 Hz, 1H, Ar-*H*); ^{1}H NMR (THF-d$_8$, 300.1 MHz, 300 K): δ *ca.* 0.4-1.3 (vbr, 18H, CH(C*H*$_3$)$_2$), 0.63 (d, br, 3H, CH(C*H*$_3$)$_2$), 0.74 (d, 3H, *J* = 6.9 Hz, 6H, CH(C*H*$_3$)$_2$), 0.66 (d, br, 3H, CH(C*H*$_3$)$_2$), 0.80 (d, br, 3H, CH(C*H*$_3$)$_2$), *ca.* 3.4-4.0 (vbr, 2H, CH(C*H*$_3$)$_2$), 3.65 (sept, *J* = 6.9 Hz, 2H, CH(C*H*$_3$)$_2$), 6.54-7.90 (m, 24H, Ar-*H*), 7.93 (d, *J* = 6.3 Hz, 1H, Ar-*H*); ^{7}Li NMR (THF-d$_8$, 155.5 MHz, 300 K): δ 1.70 (s, 2Li), 1.56 (s, 1Li); ^{13}C{^{1}H} NMR (C_6D_6, 75.5 MHz, 333 K): δ 22.9 (br, CH(*C*H$_3$)$_2$), 22.7 (br, CH(*C*H$_3$)$_2$), 22.8 (br, CH(*C*H$_3$)$_2$), 24.2-24.9 (br, several CH(*C*H$_3$)$_2$ and/or *C*H(CH$_3$)$_2$, resonances hidden by strong solvent signal), 27.8 (*C*H(CH$_3$)$_2$), 28.0 (*C*H(CH$_3$)$_2$), 118.3 (d, J_{PC} = 3.2 Hz, Ar-*C*), 119.1 (d, J_{PC} = 3.8 Hz, Ar-*C*), 122.1-122.5 (m, overlapping Ar-*C*), 122.8 (d, J_{PC} = 3.3 Hz, Ar-*C*), 124.4 (d, J_{PC} = 3.5 Hz, Ar-*C*), 125.1 (d, J_{PC} = 2.3 Hz, Ar-*C*), 126.1-126.3 (m, overlapping Ar-*C*), 126.5 (dd, $J_{PC,PC}$ = 94.7, 9.9 Hz, Ar-*C*), 127.6 (d, J_{PC} = 2.3 Hz, Ar-*C*), 130.1 (dd, $J_{PC,PC}$ = 17.2, 3.4 Hz, Ar-*C*), 131.0 (d, J_{PC} = 9.1 Hz, Ar-*C*), 131.1 (d, J_{PC} = 7.6 Hz, Ar-*C*), 133.7 (d, J_{PC} = 6.8 Hz, Ar-*C*), 139.0 (dd, $J_{PC,PC}$ = 81.2, *ca.* 2 Hz, Ar-*C*), 142.7 (d, J_{PC} = 7.6 Hz, Ar-*C*), 144.7 (br, Ar-*C*), 145.0 (d, J_{PC} = 6.2 Hz, Ar-*C*), 150.2 (d, J_{PC} = 15.6 Hz, Ar-*C*), 151.4 (d, J_{PC} = 13.0 Hz, Ar-*C*), 152.7 (dd, $J_{PC,PC}$ = 115.0, 18.0 Hz, Ar-*C*), 152.8 (dd, $J_{PC,PC}$ = 95.4, 10.4 Hz, Ar-*C*), 154.4 (dd, $J_{PC,PC}$ = 70.7 Hz, and small, not resolved, Ar-*C*), 194.4 (d, vbr, J_{PC} = *ca.* 48 Hz, Ar-*C*); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 298 K): δ 10.1 (s, sharp), 10.6 (s, sharp); ^{31}P{^{1}H} NMR (C_6D_6, 121.5 MHz, 333 K): δ 10.1 (s, less sharp), 10.2 (s, less sharp).

X-ray crystallography

Suitable crystals were mounted in silicone oil and were either measured using an Oxford Xcalibur Gemini Ultra diffractometer (**3**, **6**) with $\mathrm{Mo_{K\alpha}}$ radiation (λ = 0.71073 Å), or at the MX1 or MX2 beamlines (all other crystal structures) at the Australian Synchrotron using synchrotron radiation with a wavelength close to $\mathrm{Mo_{K\alpha}}$ radiation. All structures were refined using SHELX.[9] All non-hydrogen atoms were refined anisotropically. Semi-empirical (multi-scan) absorption corrections were performed on all datasets. Relatively low data completeness values of 94.0–95.5% (at 25.00° theta) in the crystal structures of **5**·0.25 C_6H_{14}·0.25 C_4H_8O, **8**·3 C_6H_6, and **8**·2 C_7H_8 are due to the experimental setup at the synchrotron and only one phi scan could be collected. Severely disordered solvent of crystallization has been removed from the crystal structures of **2**·4 C_6H_6, **5**·0.25 C_6H_{14}·0.25 C_4H_8O, and **7**·0.25 C_6H_{14}·0.25 C_7H_8 using PLATON/SQUEEZE.[10] An appropriate solvent quantity to the removed electron density has been added to the molecular formula and is thus included in density, *F*(000) etc, see the crystallographic information files for further details. Geometry restraints were applied in the refinement of the toluene molecules in the crystal structure of **2**·2 C_7H_8. The Li atoms in the crystal structure of **2**·4 C_6H_6 have been refined with 50% occupancy for Li1 and Li2, and 25% occupancy for Li3, Li3A, Li4 and Li4A, respectively, with half a molecule in the asymmetric unit to give a total of 4 Li per full molecule. Also in **2**·4 C_6H_6, three benzene molecules have been removed using PLATON/SQUEEZE and one benzene molecule has been refined using geometry restraints. One coordinated THF molecule in the crystal structure of **3** was disordered and was modelled with two positions for each atom (O2, C42-C45), with two parts with 64% and 36% occupancy using geometry restraints. In the structure of **8**·2 C_7H_8, two toluene molecules, and one isopropyl group (C32-C34) are disordered and were modelled with two positions for each atom with a set occupancy of 50% using geometry restraints. Li1 and Li4 were refined with 50% occupancy, Li2 and Li3 with full occupancy in the half molecule; giving a total of 6 Li per full molecule. In the crystal structure of **9**·0.25 C_6H_{14}, three coordinated THF molecules are disordered and have been modelled with two positions each for the carbon atoms C54-C57 (THF with O2) with refined occupancies of 34 and 66% for each part, two positions for the carbon atoms C115-C118 (50%) and C119-C122 (50%), and two positions for O6, C120-C126 (66%) and O6A, C127-C130 (34%). Geometry restraints have been applied to model those disordered THF molecules and the *n*-hexane lattice solvent molecule. Refinement details are summarized in Table 1 and further information can be found in the crystallographic information files. CCDC 997641-997649 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 1 Crystallographic data.

Compound reference	**2**·2 C_7H_8	**2**·4 C_6H_6	**3**	**5**·0.25 C_6H_{14}·0.25 C_4H_8O	**6**	**7**·0.25 C_6H_{14}·0.25 C_7H_8	**8**·3 C_6H_6	**8**·2 C_7H_8	**9**·0.25 C_6H_{14}
Chemical formula	$C_{112}H_{124}Li_4N_4P_4$	$C_{122}H_{132}Li_4N_4P_4$	$C_{45}H_{54}LiNO_2P_2$	$C_{63.50}H_{83.50}Li_2N_2O_{3.25}P_2$	$C_{57}H_{70}Li_2N_2O_2P_2$	$C_{61.25}H_{82.50}Li_2N_5P_2$	$C_{116}H_{124}Li_6N_4P_4$	$C_{112}H_{122}Li_6N_4P_4$	$C_{66.50}H_{88.50}Li_3N_2O_4P_2$
Formula Mass	1677.79	1805.96	709.77	1002.64	890.97	964.64	1739.71	1689.66	1062.65
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
a/Å	14.535(3)	18.743(4)	9.9994(2)	13.234(3)	14.3832(6)	12.276(3)	27.540(6)	21.829(4)	13.564(3)
b/Å	15.354(3)	34.226(7)	20.3004(3)	22.502(5)	16.9159(6)	15.641(3)	14.953(3)	19.195(4)	19.665(4)
c/Å	20.933(4)	17.098(3)	20.0691(4)	22.674(5)	21.7831(8)	19.225(4)	25.150(5)	24.702(5)	23.258(5)
α/°	95.61(3)	90.00	90.00	105.93(3)	90.00	70.31(3)	90.00	90.00	88.59(3)
β/°	90.64(3)	91.70(3)	101.269(2)	92.96(3)	105.412(4)	75.60(3)	110.97(3)	113.68(3)	88.44(3)
γ/°	93.36(3)	90.00	90.00	105.66(3)	90.00	82.25(3)	90.00	90.00	79.17(3)
Unit cell volume/Å^3	4640.6(16)	10964(4)	3995.32(13)	6194(2)	5109.3(3)	3361.0(12)	9671(3)	9479(3)	6090(2)
Temperature/K	100(2)	100(2)	123(2)	100(2)	123(2)	100(2)	100(2)	100(2)	100(2)
Space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P\bar{1}$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/c$	$P\bar{1}$
No. of formula units per unit cell, Z	2	4	4	4	4	2	4	4	4
Radiation type	Synchrotron	Synchrotron	MoKα	Synchrotron	MoKα	Synchrotron	Synchrotron	Synchrotron	Synchrotron
Absorption coefficient, μ/mm^{-1}	0.133	0.117	0.146	0.113	0.127	0.100	0.130	0.131	0.119
No. of reflections measured	95622	55786	30658	92325	28918	68465	62329	29992	125112
No. of independent reflections	26042	15595	8728	24125	8927	18781	16273	7885	34301
R_{int}	0.0694	0.0640	0.0224	0.0339	0.0470	0.0590	0.1710	0.0747	0.0680
Final R_1 values ($I > 2\sigma(I)$)	0.0516	0.0566	0.0366	0.0523	0.0591	0.0532	0.0719	0.1083	0.0566
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1235	0.1466	0.0872	0.1423	0.1507	0.1371	0.1645	0.2421	0.1406
Final R_1 values (all data)	0.0714	0.0768	0.0476	0.0629	0.0778	0.0834	0.1396	0.1264	0.0833
Final $wR(F^2)$ values (all data)	0.1339	0.1546	0.0941	0.1489	0.1648	0.1482	0.1990	0.2489	0.1558
Goodness of fit on F^2	1.027	1.051	1.028	1.031	1.060	0.971	1.013	1.332	1.026
CCDC number	997641	997642	997643	997644	997645	997646	997647	997648	997649